^{13}C NMR SPECTRUM OF COUMARIN

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UDC 541.6 + 547.64

In the solution of structural problems by the application of ^{13}C NMR spectroscopy in a broad series of natural coumarins, it is necessary unambiguously to determine the positions of the signals from the carbon atoms in the ^{13}C NMR spectrum of coumarin — the parent of this class of compound.

However, in the published NMR spectrum of coumarin [1] the positions of the signals from the C_3, C_5, and C_7 atoms were not determined and the signal from the C_6 atom was assigned incorrectly: It was ascribed a chemical shift (CS) of 116.5 ppm, while the signals from tertiary carbon atoms of unsubstituted benzene rings of heteroaromatic compounds are located in a weaker field [2]. Turner and Pirkle [11] gave only the signals from the carbons atoms of the α-pyrone ring of coumarin. In order to solve the problem posed, we have studied the ^{13}C spectra of coumarin (I), [3-D]coumarin (II), [4-D]coumarin (III), and 7-methoxycoumarin (IV) measured under conditions of complete double heteronuclear resonance with noise decoupling from protons. In the assignment of the signals we also used the characteristics of ^{13}C spectra obtained under conditions of incomplete double heteronuclear resonance.*

In the ^{13}C NMR spectrum of [3-D]coumarin (II) (Fig. 1), in place of the two adjacent signals at 116.82 and 116.46 ppm observed in the carbon NMR spectrum of coumarin (I) (in order to separate the signals from the C_3 and C_8 atoms, both spectra were taken in a nonpolar solvent), only one signal remains, at 116.38 ppm. Since the second signal is due to the C_8 carbon atom [1], the first must relate to the C_3 carbon atom of the α-pyrone ring. In [1], this signal was erroneously ascribed to the C_6 carbon atom.

The low intensity of the C_3 signal in the ^{13}C NMR spectrum of (II), not exceeding the noise level, is due to its splitting as a consequence of spin–spin coupling of the ^2H and ^{13}C nuclei and the absence for C_3 of a nuclear Overhauser effect, and also to an increase in the relaxation time of the C_3 nucleus when the hydrogen bound to it is replaced by deuterium.

In a comparison of the CS values of the corresponding signals in the ^{13}C NMR spectra of (I) and (II) (δ: 158.35; 154.07; 142.17; 131.08; 127.49; 123.64; 118.66; 116.82; 116.46 ppm and 158.55; 153.98; 142.37; 131.16; 127.64; 123.75; 118.66; 116.38 ppm), a shift of the signals in the latter as the result of the replacement of the hydrogen at the C_3 atom by deuterium is observed. The signals from the C_2 and C_4 atoms, which are present in the ortho positions to C_3 undergo a shift twice as great in absolute magnitude ($\Delta\delta = +0.2$ ppm) than the signals from the carbon atoms at a distance from it of more than one bond. Thus, the signal of the C_8 atom is shifted by $\Delta\delta = -0.08$ ppm, which confirms the correctness of its assignment in (I) and (II) to the signals at 116.46 and 116.38 ppm, respectively.

To confirm the assignment of the signal from the C_4 atom in the carbon NMR spectrum of (I) we recorded the ^{13}C NMR spectrum of [4-D] coumarin (III) (see Fig. 1). It contained signals at δ: 158.50; 153.93; 142.46; 131.24; 127.74; 123.85; 118.64; 116.41; 116.29 ppm, which

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*To simplify the terminology, O. A. Subbotin has proposed to replace the term "^{13}C spectrum obtained under conditions of complete double heteronuclear resonance" by "^{13}C spectrum of palliative [3] resonance."

M. V. Lomonosov Moscow State University Scientific-Research Institute of Pharmacology, Academy of Medical Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No.4, pp. 458-462, July-August, 1975. Original article submitted May 5, 1974.

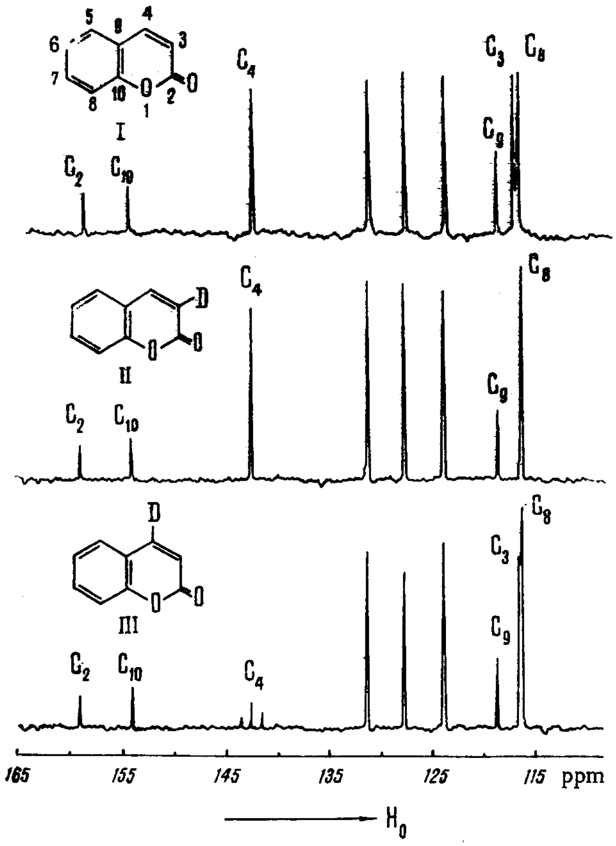

Fig. 1. ^{13}C NMR spectra of coumarin (I) and of 8-methoxycoumarin (IV) in DMSO.

are singlets (with the condition of noise decoupling from the protons), apart from the signal at 142.46 ppm. The latter is a triplet with a spin–spin coupling constant (J = 25.2 Hz) characteristic for the coupling of ^{2}H and ^{13}C nuclei [4]. In the ^{13}C NMR spectrum of (I) it is represented by a signal at 147.17 ppm which, consequently, is due to the C_4 carbon atom, in agreement with its assignment given in Johnson and Jankowski's book [1].

The shift of this signal in the carbon NMR spectrum of (III) by $\Delta\delta = +0.3$ ppm is due to the α effect on isotopic substitution and its value is close to that of the same effect in deuterated benzenes [5]. The maximum shift in absolute value of $\Delta\delta = -0.41$ ppm is undergone by the signals from the C_3 atom, and it is four times greater than the shift of the signals due to the β effect in deuterobenzenes [5] and has the opposite sign. It must be mentioned that although the C_5 carbon atom, just like the C_3 atom, is present in the ortho position to the C_4 carbon atom, its signal in the spectrum of [4-D]coumarin (III) is shifted by an anomalously small amount ($\Delta\delta = -0.02$ ppm).

The positions of the signals from the C_5, C_6, and C_7 atoms in the ^{13}C NMR spectrum of coumarin (I) were determined with the aid of the carbon NMR spectrum of 7-methoxycoumarin (III) (Fig. 2). The presence in this compound of a methoxy group on the C_7 atom enables the problem posed to be solved by using information on the α, the ortho, the meta, and the para effects from the O–CH_3 group in the ^{13}C NMR spectrum of anisole.

The spectra of substances (I) and (IV) obtained in a polar solvent (to increase the concentration of the latter substance) contain signals at the following values of δ: for (I) – 159.70; 153.31; 143.73; 131.56; 128.11; 124.11; 118.51; 115.97 and for (IV) – 162.40; 160.17; 155.35; 144.11; 129.31; 112.37; 112.28; 112.18; 100.60; 55.78 (OCH_3). Considering the values of the effects mentioned in anisole, which are, respectively, $\Delta\delta(\alpha) = +30.2$ ppm, $\Delta\delta(\text{ortho}) = -14.7$ ppm, $\Delta\delta(\text{meta}) = +1.0$ ppm, and $\Delta\delta(\text{para}) = -7.8$ ppm [6], it may be concluded that the smallest paramagnetic shift in the ^{13}C NMR spectrum of (IV) in comparison with the spectrum of (I) must be undergone from the signal of the C_5 atom as a result of the meta effect. This condition in the carbon NMR spectrum of (I) (see Fig. 2) can be satisfied only by the signal at 128.11 ppm, since in the spectrum of (IV) there is only one signal in this region,

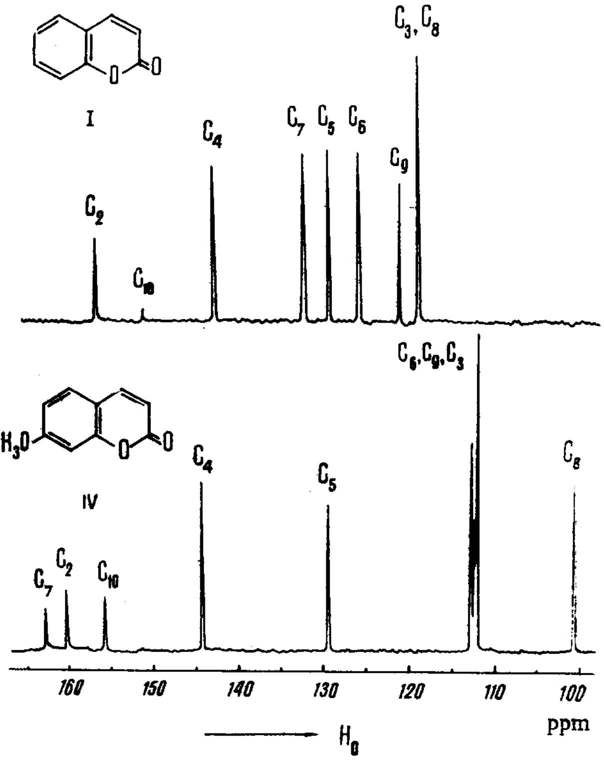

Fig. 2. ^{13}C NMR spectra of coumarin (I), [3-D] coumarin (II), and [4-D]coumarin (III) in CCl_4.

at 129.31 ppm, and the effect mentioned for the C_5 atom is close to the expected value, $\Delta\delta$ = +1.2 ppm.

The greatest downfield shift due to the α effect will be observed from the signal from the C_7 carbon atom. In view of the fact that the paramagnetic shift of the signal from C_4 in the spectrum of (IV) — +0.38 ppm — is approximately of the same magnitude, one must expect a downfield shift of the signal from the C_2 atom, the CS of which in the ^{13}C NMR spectrum of (IV) should be 160.17 ppm. Consequently, the signal from the C_7 atom in the spectrum of (IV) is at 162.40 ppm (a shift of the signal from the C_{10} atom* as a result of the meta effect greater by an order of magnitude than the expected value is also excluded. In the ^{13}C NMR spectrum of (I) this atom must be represented by the signal at 131.56 ppm, since in this case the value of its shift by $\Delta\delta$ = +30.84 ppm is closest to the value of the α effect in anisole.

In the carbon NMR spectrum of (I) the signal from C_6 is located at 124.11 ppm; the CSs of C_5 and C_7 in it are shown above. Consequently, in view of the magnitude of the ortho effect in anisole, this atom must be represented in the spectrum of (IV) by one of two signals: at 112.37 and at 112.18 ppm (the signal at 112.28 ppm remains a singlet under the conditions of incomplete double heteronuclear resonance and is assigned to the C_9* atom). Hence the shift of the C_6 signal in the ^{13}C NMR spectrum of (IV) is $\Delta\delta = -(11.83 \pm 0.1)$ ppm and is 2.7 ± 0.1 ppm in absolute value less than the corresponding effect in anisole. Conversely, the ortho effect for the C_8 atom in the carbon NMR spectrum of (IV), the signal of which is located at 100.6 ppm, is 0.67 ppm in absolute value greater than the expected effect, which can be explained by the different locations of the C_6 and C_8 atoms in relation to the oxygen atom of the lactone ring in the coumarin nucleus.

Thus, the signals from the C_5, C_6, and C_7 carbon atoms of the benzene ring in the ^{13}C NMR spectrum of coumarin (I) (see Fig. 2) are located at 128.11, 124.11, and 131.56 ppm, respectively.

The results of a comparison of the values of the ^{13}C CSs found for coumarin (I) with the π-electron densities on its atoms obtained by the MOH and the PPP methods [7, 8] show that

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*For positions "9" and "10" in the coumarin nucleus, see the system of numbering shown in Fig. 1 — Consultants Bureau.

there is no strict correlation between these magnitudes: In the first case there is no correlation for the C_{10} and C_3 atoms, and in the second for the C_{10}, C_8, and C_3 atoms. For 7-methxycoumarin (IV) no such relationship whatever is observed. Consequently, the assignment of the signals in the ^{13}C NMR spectra of coumarin and its derivatives based on the relation $\delta\ ^{13}C = k \cdot q_{\pi}$ cannot be conclusive, and the solution of this problem must be obtained by experimental methods.

EXPERIMENTAL METHOD

Substances (I-III) were synthesized as described previously [9]. Compound (IV) was isolated from the plant *Artemisia silvatica.* The purity of substances (I-IV) was determined by thin-layer chromatography on Al_2O_3, and their structures were identified by PMR spectroscopy.

The ^{13}C NMR spectra of (I-IV) were obtained on a standard Varian XL-100-15 spectrometer under pulse conditions of accumulation with Fourier tranformation. Saturated solutions were used for recording: (I-III) in CCl_4 and (I) and (IV) in DMSO. The chemical shifts were measured with an accuracy of 0.04 ppm relative to the internal signal of the solvent (δ_{CCl_4} = 95.99, δ_{DMSO} = 40.48 ppm followed by recalculation to the TMS scale [10].

SUMMARY

The positions of the signals from the C_3, C_5, C_6, and C_7 carbon atoms in the ^{13}C NMR spectrum of coumarin have been established with the aid of information obtained from the ^{13}C NMR spectra of [3-D]-, [4-D]-, and 7-methoxycoumarins and by the use of an additive calculation based on the increments of the methoxy group in the ^{13}C NMR spectrum of anisole.

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